

NASA TTF-10,220

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Translation of "Opredeleniye Davleniya Nasyschennogo Para Dvuokisi Niobiya."

Doklady Akademii Nauk SSSR, Vol. 145, No. 1, pp 119-121, 1962.

NASA TTF-10,220

N66 33679

FACILITY FORM 802

(ACCESSION NUMBER)

(THRU)

(PAGES)

(CODE)

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 1.00

Microfiche (MF) 1.50

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. JUNE 1966

DETERMINATION OF THE SATURATED VAPOR PRESSURE OF NIOBIUM DIOXIDE

S.A. Shchukarev, G.A. Semenov, and K.Ye. Frantseva

(Presented by Academician A.N. Terenin, March 3, 1962)

ABSTRACT

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The vapor pressure of niobium dioxide is determined using the Knudsen effusion method. The cylindrical effusion chamber and the associated apparatus are described. The computed dissociation energy of NbO_2 is $14.9 \pm .1$ volts.

One study (Ref 1) has measured the vapor pressure of niobium dioxide./119^{*}
The authors of this study employed the effusion method of Knudsen and obtained several values for the vapor pressure in the $1489\text{--}1905^\circ\text{K}$ temperature range. It was found in other studies (Ref 2, 3) that NbO_2 has significant volatility at $1650\text{--}1700^\circ$, and at $1850\text{--}1900^\circ$ the vaporization rate of this oxide is quite large. We have previously reported (Ref 4) on the vaporization of NbO_2 by the mass-spectrometer method. The vapor composition above niobium dioxide, when it was vaporized from an open surface, was found in this case, and it was determined that NbO_2 vaporizes without dissociating. By measuring the temperature dependence of ion currents, we were able to compute the sublimation heat of NbO_2 , equaling 142 ± 3 kcal/mole, for a $1500\text{--}1880^\circ\text{K}$ temperature range.

In this study we have measured the vapor pressure of niobium dioxide by the Knudsen effusion method, employing a differential variation of the method which is similar, for example, to that described in (Ref 5,6). A cylindrical,

*Note: Numbers in the margin indicate pagination in the original foreign text.

effusion chamber was made of forged molybdenum (Figure 1). It consisted of the main body (1) and the cover (2) with an effusion opening whose diameter was 0.308 mm. The ratio between the surface of the substance being volatilized and the surface of the effusion opening was 500:1. There was an opening in the lower part of the main body; a thermocouple (3), which was made of tungsten-rhenium alloys containing 5 and 20 percent rhenium (Ref. 7), was attached to the opening by the screw (4). The thermocouple was calibrated by the readings of the first-class, optical pyrometer in the High Temperature Laboratory of the Mendeleyev All-Union Scientific Research Institute of Meteorology. The temperature was also measured by the pyrometer, which was focused on the junction of the thermocouple through a narrow channel which passed through the lower portion of the main body of the chamber, and which was tested in the laboratory of the same institute by using a second-class temperature lamp. The effusion chamber was heated by electron bombardment. The current stabilization of the cathode emission and the high voltage made it possible to keep the chamber temperature sufficiently constant ($\pm 2^\circ$). The effusion chamber was covered by tantalum radiation screens and by a water jacket. The sublimate was condensed on targets which were cooled by liquid nitrogen and which could be replaced by means of a magnetic plunger. The all-metal effusion device made it possible to obtain a vacuum on the order of $1 \cdot 10^{-5}$ mm Hg at an operational chamber temperature of 2100° K.

A pentoxide, which was tagged with the radioactive isotope Nb^{95} , was used as the original preparation for obtaining the niobium dioxide. According to data derived from spectroanalysis, it contained 0.24 percent admixtures. Niobium pentoxide was reduced to NbO_2 with hydrogen at a temperature of 1000° for three hours. The composition of the product obtained was $\text{NbO}_{2,008}$, as was

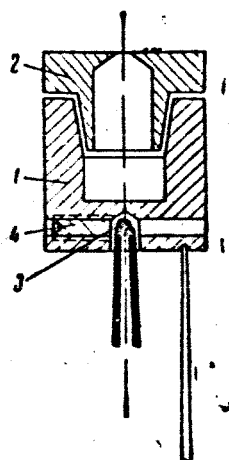


Figure 1

Effusion Chamber

- (1) - main body; (2) - cover; (3) - thermocouple;
(4) - screw for attaching thermocouple

determined by the weight increase during calcination. The X-ray photograph of the sample corresponded to data in the literature (Ref. 8).

By initially measuring the silver vapor pressure and by obtaining results which did not differ by more than 10 percent from those given in the literature (Ref. 9), we were then able to measure the vapor pressure of NbO_2 . The results obtained are presented graphically in the form of the line 1 (Figure 2), which is described by the following equation:

$$\lg P = -\frac{30300}{T} + 12,42 \text{ mm.}$$

The sublimation heat of NbO_2 , computed from the inclination of the line 1, equaled 138 ± 2 kcal/mole. The line 2 represents data from the work (Ref. 1). The sublimation heat which we computed from the inclination of this line comprised 37.5 kcal/mole. Obviously, this quantity is erroneous. Table 1

TABLE 1
VAPOR PRESSURE AND THERMODYNAMIC FUNCTIONS OF NIOBIUM DIOXIDE

No.	Temp. °K	P, mm	solid cal/mole . degree			gaseous cal/mole . degree			$-\Delta\phi^*$	ΔH_0 , Subl. kcal/mole
			$\frac{F_T^0 - H_{298}^0}{T}$	$\frac{H_{298}^0 - H_0^0}{T}$	$\frac{F_T^0 - H_0^0}{T}$	$\frac{F_T^0 - H_{298}^0}{T}$	$\frac{H_{298}^0 - H_0^0}{T}$	$\frac{F_T^0 - H_0^0}{T}$		
			T	T	T	T	T	T		
1	1938	$6.02 \cdot 10^{-14}$	30.25	1.19	29.06	75.45	1.41	74.04	44.98	141.3
2	1948	$8.27 \cdot 10^{-14}$	30.31	1.18	29.13	75.53	1.40	74.13	45.00	140.7
3	1978	$1.22 \cdot 10^{-3}$	30.48	1.16	29.32	75.76	1.38	74.38	45.06	140.5
4	1978	$1.17 \cdot 10^{-3}$	30.48	1.16	29.32	75.76	1.38	74.38	45.06	141.7
5	1992	$1.51 \cdot 10^{-3}$	30.56	1.16	29.40	75.84	1.37	74.47	45.07	141.7
6	2005	$2.16 \cdot 10^{-3}$	30.63	1.15	29.48	75.93	1.36	74.57	45.09	141.2
7	2031	$3.19 \cdot 10^{-3}$	30.77	1.13	29.64	76.07	1.34	74.73	45.09	141.5
8	2037	$3.22 \cdot 10^{-3}$	30.81	1.13	29.68	76.11	1.34	74.77	45.09	141.9
9	2081	$7.55 \cdot 10^{-3}$	31.05	1.11	29.94	76.35	1.31	75.04	45.10	141.4
10	2122	$1.12 \cdot 10^{-2}$	31.33	1.08	30.25	76.58	1.29	75.29	45.04	142.5

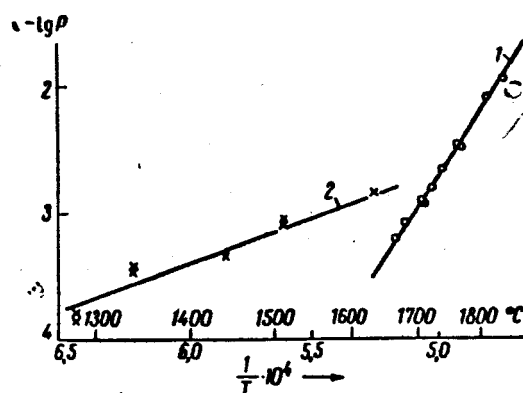


Figure 2

Vapor Pressure of Niobium Dioxide

(1) - experimental data; (2) data of Golubtsov, et al. (Ref. 1)

presents data which are requisite for computing the sublimation enthalpy of $\Delta H_0^0[\text{NbO}_2]$. In order to compute the change in Gibbs free energy $\Delta\phi^*$ during sublimation of NbO_2 , we employed data regarding the temperature dependence of the function of $-\frac{F_T^0 - H_{298}^0}{T}$ and the enthalpy difference $H_{298}^0 - H_0^0$ for condensed (Ref. 10,11) and gaseous (Ref. 12) NbO_2 . By knowing $\Delta\phi^*$, by means of equation

$$\Delta H_0^0 = -RT \ln P - \Delta \Phi^* T$$

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we were able to obtain the sublimation heat $\Delta H_0^0 = 141 \pm 0.4$ kcal/mole. By taking the following quantities from sources in the literature: heat of formation $\Delta H_{298}^0 = -191.7$ kcal/mole (Ref. 13), an enthalpy difference $H_{298}^0 - H_0^0 \approx 2300$ cal/mole (Ref. 10) for condensed NbO_2 , as well as the sublimation heat of metallic Nb $\Delta H_0^0 = 171.8$ kcal/gram-atm (Ref. 14) and the atomization heat of oxygen $\Delta H_0^0 = 118.0$ kcal/mole (Ref. 15), we were able to compute the dissociation energy of a gaseous molecule of NbO_2 , which was found to equal 14.9 ± 0.1 electron volts.

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Received February 27, 1962

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